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COMPARATIVE RHEOLOGICAL AND FRACTURE PROPERTIES OF EPOXY RESINS IN THE GLASS TRANSITION REGION

by

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Contribution No. ____

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19960424 051

The Glass Transition

Two transition regions are important in determining the solid state properties of high polymers. These are the amorphous state glass transition (T_g), also identified as the second order transition, and the crystalline to amorphous transition normally termed the crystalline melting or first order transition. These transitions are depicted, in simplified form, in Figure 1 in terms of the specific volume versus temperature functions. With crystallizable polymers the crystalline melting temperature (T_m) always occurs at the higher temperature and involves, over a very narrow temperature range, a discontinuity in the specific volume - temperature function, thus the term first order transition. Many polymers, due to lack of regularity in main chain structure, do not display a capability to crystallize. Others, although crystallizable, may be cooled to below the glass transition temperature (T_g) in essentially noncrystalline form due to slow rates of crystallization. The glass transition ideally produces

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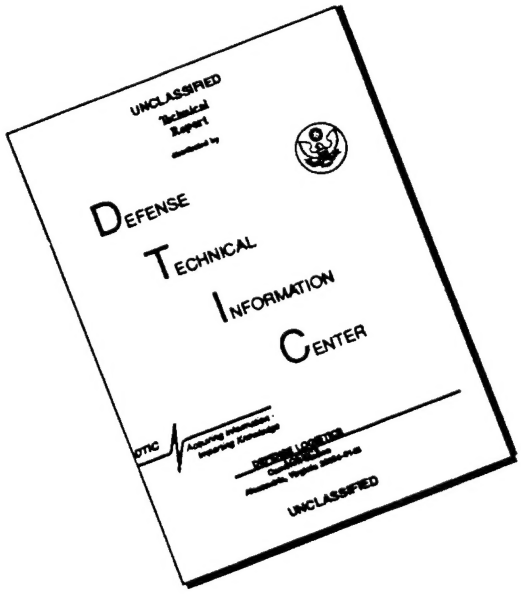

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a discontinuity in the derivative (dV/dT) of the specific volume versus temperature function thus providing the term second order transition.

Figure 1 indirectly identifies the fundamental reason why physical properties change abruptly at T_m and much more gradually at T_g. Doolittle[1] has shown for a number of liquids the temperature dependence of viscosity to be a function of the molecular free volume. More recently Williams, Landel and Ferry[2] have applied this explanation to the viscoelastic properties of high polymers. Ferry and Stratton[3] have recently reviewed and extended this concept to account for effects of temperature, concentration, hydrostatic pressure, and tensile strain in the region of the glass transition. Following these arguments, we may conclude that free volume is abruptly changed at the crystalline melting temperature producing sharp changes in physical properties. Following the evidence of Williams, Landel and Ferry,[2] the free volume is a constant value below the glass transition, occupying a volume fraction $f_g = 0.025$, and above the glass transition increases by an amount $(T - T_g)\Delta\alpha$ where $T_g < T < T_g + 100°K$ and $\Delta\alpha$ is the change in expansion coefficient at the glass transition. The continuous and gradual change in free volume produces the continuous and gradual changes in physical properties over a rather broad temperature range above T_g.

Time-Temperature Superposition

The principles of time-temperature reduced variables as they apply to rheological and fracture properties of high polymers at temperatures from T_g to T_g + 100(°K) provide a means of consolidating measurements from several temperatures to a single reference temperature.[4] These temperature reduced "master curves" provide an ideal device for comparing properties of polymers at equivalent reduced thermodynamic and rheological states. This device should permit the direct comparison of rheological and fracture properties of a typical elastomer, thermoplastic resin, and thermoset epoxy based upon considerations of chemical composition and molecular architecture.

The two assumptions of the reduced variables treatment as it applies to rheological and fracture properties are that:

1. Both modulus and true stress are proportional to absolute temperature and density as required by the kinetic theory of elasticity.
2. All molecular relaxation and fracture processes are shifted by the same time or frequency ratio (a_T) by temperature change and thus can be represented at that temperature (T) by a single apparent activation energy of flow (A).

Figure 2 presents the equations which define these assumptions and an identification of terminology.

A refinement of the second assumption has evolved from the work of Williams, Landel and Ferry which has expression in the

familiar WLF equation.[2] A statement and functional form for this equation is illustrated in Figure 3. This expression provides a nearly universal form for the function of (a_T) versus temperature (T) at temperatures from T_g to T_g + 100°K. The temperature T_s of the WLF equation is the temperature at which (a_T) = 1, and for a large number of high polymers $T_s = (T_g + 50) \pm 5°K$. The polymers included in this comparative study conform in both rheological and fracture response to both the reduced variable assumptions and the criteria of the WLF equation where $T_s = T_g + 50°C$. The WLF equation is derived from the previously discussed concept of molecular free volume and at T_s the materials discussed here could be viewed as having equivalent fractional free volumes.

We shall select 296°K or 23°C. as the arbitrary temperature for reducing modulus and stress to thermodynamically equivalent states in conformance with the first assumption of reduced variables. The reduced time (t/a_T) or reciprocal frequency ($1/wa_T$) scales will be reduced to $T_g + 50(°K) = T_s$ for all rheological and fracture data. This convention on time reduction presents the data at rheological equivalent states in terms of fractional free volume and also conveniently places unit time in a time sensitive region of rheological and fracture response.

Having reduced our data to approximately equivalent states of molecular free volume, we may now evaluate our rheological and fracture master functions in terms of comparative abilities

of molecular mobilities to utilize these vacancies. Monomer chemical composition and structure will dictate short time response. Macromolecular architecture, molecular weight and crosslinking density dominantly control long time response.

Comparative Dynamic Mechanical Properties

The three materials compared in this study:

	Material	T_g(°K)
(A)	SBR Elastomer (butadiene:styrene copolymer -20 to 23% bound styrene)	210
(B)	Polyvinyl chloride	346
(C)	Epoxy resin (stoichiometric copolymer of the diglycidyl ether of Bisphenol-A and methylene bis (orthochloroaniline))	388

represent commercially important members of three classes of high polymers which are respectively elastomers, thermoplastic resins, thermosetting resins. Elastomers, including SBR, are characterized by long, flexible main chains in conjunction with weak secondary forces of interaction. Amorphous thermoplastic resins either display stiff main chains or strong secondary bonding. Polyvinyl chloride is primarily dependent upon the polar interchain attractions to provide its characteristic thermoplastic resin behavior. Amorphous thermosetts generally display rigid main chains, strong secondary attraction and a highly crosslinked space network. The epoxy resin discussed here displays all three of these criterias typical of amorphous thermosetts.

The dynamic properties of SBR elastomer,[5] polyvinyl chloride[6] and epoxy resin[7] are taken from the literature. The epoxy resin considered here is selected from a larger group of typical diamine crosslinked epoxy polymers previously examined with regards to the interrelation of the glass transition and dynamic mechanical response.[8] The reduced data are represented in the fashion already described. The dynamic properties are identified by the following equations:

$$E^* = E' + iE''$$

$$\tan \delta = E''/E'$$

where E^* is the dynamic Young's modulus, (E') the storage (in phase) modulus, (E'') the loss (out of phase) modulus and $i = (-1)^{1/2}$. The ratio of loss to storage modulus is a dimensionless term denoted as the loss tangent ($\tan \delta$).

Plots of the reduced storage modulus ($296\ E'/T$) versus reduced reciprocal frequency ($1/wa_T$) for these three polymers are presented in Figure 4. It may be noted that the modulus values decrease by several orders of magnitude from the short time glassy state to the long time rubbery state response. This dramatic decrease in modulus is typical of all amorphous high polymers in the glass transition region. The transition from glassy state to rubbery state is accomplished through a broad range, normally 6 to 10 logarithmic decades, of reduced reciprocal frequency. This broad time range for the glass-rubbery state transition is due to a gradual unfreezing of a

spectrum of molecular mobilities. For the SBR elastomer this transition in modulus would be associated with a low temperature freezing or embrittlement and for the polyvinyl chloride and epoxy resin would be associated with a high temperature softening or heat distortion temperature as identified by standard test techniques.

Figure 4 indicates this molecular unfreezing to occur at much lower reciprocal frequencies or shorter times for the SBR elastomer. This may be attributed to the much greater short segment mobility due to random addition of the butadiene and styrene comonomer units in conjunction with low intermolecular binding forces. In other words, SBR elastomer short segments can more effectively utilize the additional molecular free volume than can those of the PVC and epoxy resin short segments.

The storage modulus master curve for the epoxy resin displays a single smooth transition between the glassy state response at reciprocal frequencies less than 10^{-8} sec. to an equilibrium network elastic response at reciprocal frequencies greater than 10^{3} sec. The master curves for both SBR and PVC display similar major transitions from the glassy state. In the rubbery response region, however, both SBR and PVC give evidence of an initial equilibrium then further decline in magnitude of reduced storage modulus (E' 296/T) with increased time or reciprocal frequency. This distinctive feature of the SBR and PVC rubbery response is attributed to a pseudo-equilibrium response due to chain entanglements. Since neither

the SBR and PVC sample of Figure 4 are chemically crosslinked, this entanglement effect gradually disappears and, as the data indicate, we proceed with increased time or reciprocal frequency into a second transition from a rubbery to viscous liquid state.

This discussion of transitions in rheological state from glassy to rubbery and subsequent liquid regions of response with increased response time or reciprocal frequency leads naturally to the presentation of the loss tangent ($\tan \delta$) master curves of Figure 5 which complement the reduced storage modulus curves of Figure 4. The loss tangent ($\tan \delta$) function exhibits a maximum in regions where the dynamic modulus (E^*) changes most rapidly. The loss tangent ($\tan \delta$) function is then an excellent parameter to gage the intensity of rheological change in state.

Inspection of Figure 5 reinforces the comments already made concerning the reduced storage modulus (E' 296/T). The major maximum in loss tangent ($\tan \delta$) is evidenced for SBR at shorter times than for PVC and the epoxy resin. The epoxy resin loss tangent ($\tan \delta$) function displays a single maximum evidencing a single transition from the glassy to equilibrium rubbery state. Both SBR and PVC display major maxima associated with the glass to rubbery transition and in addition exhibit evidence of an approach to a second maximum at the long time or high reciprocal frequency limits of measurement. This approach to a second maximum is, as previously discussed, associated with the rubbery to liquid state transition for SBR and PVC.

These master functions of dynamic mechanical response have an additional practical significance in the direct evaluation of materials in vibration damping. The mechanical energy or work dissipated in a unit volume of material per cycle (W) is given by the following equation:

$$W = \pi \gamma_o^2 E'' = \pi S_o^2 \frac{E''}{E^{*2}}$$

where (γ_o) is the maximum amplitude strain and (S_o) maximum amplitude stress of the sinusoidal dynamic stress-strain cycle.

Comparative Tensile Properties

Tensile properties measurements yield three master functions of polymer response. The first of these is the reduced tensile relaxation modulus (E_t) which to a first approximation[9,10] is analogous to the dynamic storage modulus (E') where the reduced times of the tensile relaxation and dynamic experiment are equivalent, that is (t/a_T) = ($1/wa_T$). The relaxation modulus master function completely defines the deformation properties in the glass transition region and from it one may reconstruct the stress-strain curve for any condition of that temperature and tensile strain rate.

In conjunction with the deformation properties, a complete description of tensile properties requires definition of true fracture stress $(\alpha S)_b$ and fracture strain γ_b. These properties fix the end point of any tensile test whose deformation properties are defined by the relaxation modulus function (E_t). The true fracture or ultimate stress is defined in terms of the product

of stress (S) based upon original cross section area and the extension ratio (α) which, assuming constant volume during extension, corrects for cross section area reduction by tensile deformation and yields $(\alpha S)_b$, the stress at break based on true cross section area. The fracture or ultimate strain (γ_b) is simply the ratio of change in gage length to original gage length at break.

The tensile properties discussed here for the epoxy resin and SBR elastomer are taken from published data.[7,11] The data for the polyvinyl chloride polymer are from unpublished experiments.[12] The experimental method involves tests conducted at systematically incremented temperatures and constant strain rates with analysis of data, in terms of the theory of linear viscoelasticity, following the method of Smith.[11,13]

The data are treated, following the previous convention for dynamic properties, such that the magnitudes of E_T and $(\alpha S)_b$ are reduced to a uniform base temperature at 296°K. The reduced time base (t/a_T) for both deformation and fracture is referenced to $T_g + 50(°K) = T_s$, in conformance to this convention.

The chemical compositions and glass transition temperatures for the three polymers for which tensile properties are described in this section are similar to those previously discussed. The molecular architecture in terms of weight average molecular weight $\bar{M}_w$ and weight average molecular weight between crosslinks $\bar{M}_c$ are, however, better described for the tensile specimens as

tabulated below for the polymers involved in tensile studies:

Polymer	$\bar{M}_w$	$\bar{M}_c$	Ref.
SBR	∞	9250	(11)
PVC	$1.12 \cdot 10^6$	∞	(12)
Epoxy	∞	770	(7)

The previously discussed dynamic data for SBR elastomer are taken from a polymer which is uncrosslinked but with a high molecular weight estimated in the range $\bar{M}_w = 1.0 \cdot 10^6$.[5] This molecular structure difference for the SBR elastomer uncrosslinked and crosslinked for dynamic and tensile measurement respectively, should modify deformation and fracture properties only in the long time rubbery to liquid state transition region.

The molecular weight of the polyvinyl chloride sample for which dynamic response has been discussed is unspecified.[5] Assuming it to be of high molecular weight, as with the SBR elastomer, property differences which would constrain a direct comparison of dynamic and tensile properties would appear only in the rubbery to liquid state transition region.

The molecular structure, as indicated in the literature for the epoxy resin under discussion, is similar for both dynamic and tensile test specimens.[7] With these differences in molecular structure clearly in mind, then, let us proceed to an inspection of the tensile properties of these three polymers and possible correlation to the previously evaluated dynamic properties.

Figure 6 presents the temperature reduced relaxation modulus ($296\ E_t/T$) versus reduced deformation time (t/a_T) responses for these three polymers. In the region of short times ($\log t/a_T < -6$), as previously indicated in dynamic response, SBR elastomer preserves its rubbery properties while the PVC and epoxy modulus values increase to typical glassy state levels. Tensile measurement requires higher strain amplitudes than dynamic measurement with consequent non-linear viscoelastic effects near the glassy state. For this reason precise measurement of relaxation modulus, as the curves of Figure 6 indicate, is possible only in the lower branch of the glassy to rubbery state transition.

In the long-time response region, the crosslinked network of the epoxy provides a time independent equilibrium modulus response. This equilibrium modulus is associated with the weight average molecular weight between crosslinks by the following equation:

$$M_c = \frac{3\rho RT}{E}$$

where ρ is density, R the gas constant, T the absolute temperature, and E the equilibrium modulus. The presence of a crosslinked network for the SBR elastomer is quite evident in the stabilization of the magnitude of E_t at long times. Taking the reported values[10] of $\bar{M}_c = 9250$ and $\rho = 0.98$, we may calculate an equilibrium $E_t = 114$ psi at $T = 296°K$ from the above equation. This equilibrium (E_t) for SBR elastomer is achieved at long times greater than $\log (t/a_T) = 10$ the extreme time indicated in Figure 6.

Except for the accountable difference in SBR properties, there is a good agreement between the dynamic storage modulus (296 E'/T) and relaxation modulus properties of these three polymers.

Upon casual observation, the fracture stress functions of Figure 7 for these three classes of polymer under discussion bear a superficial resemblance to the dynamic storage modulus (E') or tensile relaxation modulus (E_t) functions of Figure 4 and Figure 6 respectively. Closer inspection indicates, however, that the glassy state values of reduced true fracture stress (296 $(\alpha S)_b/T$) persist into time regions where the modulus (E' or E_t) is changing quite rapidly. Also in the region of rubbery response where the moduli E' or E_t may have achieved equilibrium, and this is particularly noticeable for the epoxy data, the fracture stress function remains time dependent.

Upon comparing fracture stress properties for the three materials, one notes a superior strength for PVC at short times which sharply diminishes due to lack of long range molecular structure, such as provided by a crosslinked network, at the longer fracture times (t_b/a_T). SBR has intermediate fracture stress values at short times and superior values at the long time extremes of measurement. The superior fracture stress of SBR elastomer at long times is probably due to both a crosslinked structure and the very flexible main chains which best utilize this structure.

This point of necessity in having both a permanent network coupled with chain flexibility is demonstrated from the fracture stress function for the epoxy resin. Several molecular theories of polymeric tensile strength in the rubbery state demonstrate that increasing the concentration of crosslinks beyond a critical value diminishes tensile strength primarily due to the loss of the highly elastic character of the main chain segments.[14,15] The epoxy resin, with its inherently stiff main chain structure, is probably further hindered in achieving high fracture stress values by the imposition of a high density of crosslinks which further inhibit a high segment mobility in the rubbery state.

These latter points concerning the function of the permanent network structure and residual network segment mobility in the glass to rubber transition region are further amplified by the master functions of ultimate strain (γ_b) versus reduced fracture time (t_b/a_T) presented in Figure 8. The fracture strain of SBR elastomer achieves high magnitudes typical of elastomers at very short times due to inherent short segment flexibility which also influences short time modulus properties. This high fracture strain level is maintained to very long times for SBR due to the stabilizing effect of the network and high segment mobility between crosslinks.

The PVC polymer achieves highly elastic deformability in a narrower range of time in the intermediate rubbery state. Lacking a permanent structure to stabilize this property, the (γ_b) values are minimized at long times.

The epoxy resin displays a typical maximum in ultimate strain (γ_b) response in the region of the glass to rubbery state transition. However, short segment steric hinderances, which operate at short times near the glassy state, and lack of main chain mobility between corsslinks at long times prevent typical elastomeric deformability in the region of maximum (γ_b) response as shown in Figure 8.

In comparing the fracture strain (γ_b) and reduced true fracture stress ($296\ (\alpha S)_b/T$) functions of Figure 8 and Figure 7 respectively, it may be noted that maximum fracture strain occurs where fracture stress is most time dependent. This interrelation of fracture strain and fracture stress properties has its close analogy in the previously discussed interdependency of the dynamic modulus (E*) and dynamic loss tangent ($\tan \delta$).

Summary

An objective of this discussion has been to introduce a general means of referencing the temperature and time dependencies of polymeric rheological properties to provide direct comparison of dissimilar classes of polymers purely on the basis of chemical composition and polymeric structure. This referencing has been accomplished on the basis of a novel application of the well-known time-temperature reduced variables technique.

By this method it is possible to compare the microstrain responses involved in dynamic mechanical measurement to the macrostrain responses involved in tensile deformation and fracture.

This connection between the dynamic and tensile experiment is provided by the first approximation identity of dynamic storage modulus (E') to the tensile relaxation modulus (E_t) where the respective reduced reciprocal frequency ($1/wa_T$) and tensile deformation time (t/a_T) are equivalent. The fact that the tensile relaxation modulus is also the modulus at fracture where the reduced tensile deformation time (t/a_T) is equivalent to the reduced tensile fracture time (t_b/a_T) extends this correlation of dynamic response to include fracture response, assuming that linear viscoelastic deformation extends to include fracture.

The method of time-temperature reduced variables assumes as a criteria the kinetic theory of elasticity and linear viscoelastic response. It follows, then, that where data may not be superimposed to "master response curves" by reduced variables they may not be compared by the reference system of this discussion.

For amorphous polymers such as SBR elastomer, a PVC thermoplastic and epoxy thermosett, as the discussion has intended to indicate, this referencing and correlation may be quite illuminating. General statements relating response to polymer structure appear to apply quite well to dynamic, tensile deformation, and tensile fracture properties. Understanding the interrelation of general mechanical response and structure is a means of better utilizing available polymer properties. This type of understanding is a necessary prerequisite to intentional designing of polymer properties based upon chemical composition and structure considerations.

Synopsis

The rheological and fracture properties of technically and commercially important representatives of three classes of high polymers, elastomer (SBR), thermoplastics (PVC), and thermosetts (epoxy resins) are directly compared in terms of response "master" functions in the region from glassy state through rubbery state. Application of the time-temperature reduced variables treatment reduces the magnitudes of response to thermodynamically equivalent states at 296°K. The rheological time scale of response is reduced to equivalent states of molecular fractional free volume, from a further consideration of reduced variables, fixed by convention at T_g + 50°K where T_g is the glass transition temperature of the particular polymer. The dynamic properties, in terms of the storage modulus (E') and loss tangent (tan δ) and tensile properties, in terms of a relaxation modulus (E_t), the true fracture stress $(\alpha S)_b$ and fracture strain (γ_b), are qualitatively compared and discussed from the standpoint of chemical composition and macromolecular architecture. The interrelations between micro-strain dynamic properties and macrostrain tensile deformation and fracture properties are identified.

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FIGURE 1

GLASS TRANSITION & CRYSTALLINE MELT TRANSITIONS

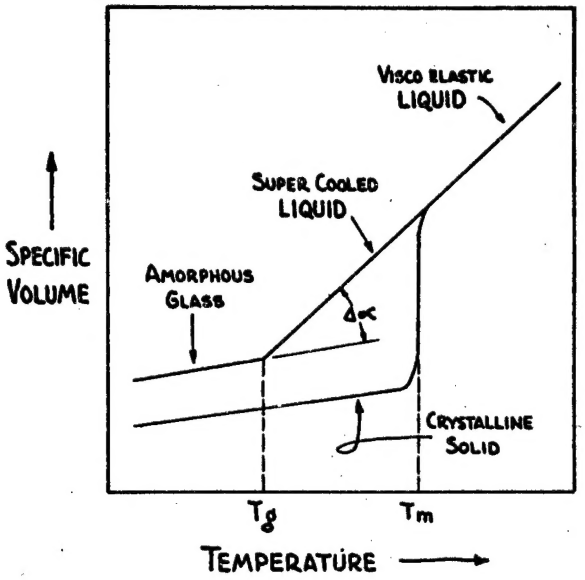

FIGURE 2

ASSUMPTIONS OF REDUCED VARIABLES

ASSUMPTION Nº 1

$$(1)\quad E_0 = E\,\frac{T_0 P_0}{T P}$$

$$(2)\quad (\alpha S)_0 = (\alpha S)\,\frac{T_0 P_0}{T P}$$

ASSUMPTION Nº 2

$$(3)\quad \log a_T = \frac{.434\,A}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

E_0, E = MODULUS AT T_0 AND T
P_0, P = DENSITY AT T_0 AND T
$(\alpha S)_0$, (αS) = TRUE STRESS AT T_0 AND T
a_T = TIME OR FREQUENCY RATIO
A = APPARENT ACTIVATION ENERGY OF FLOW
R = GAS CONSTANT
T_0 = REFERENCE TEMPERATURE (°K)
T = TEST TEMPERATURE (°K)

FIGURE 3

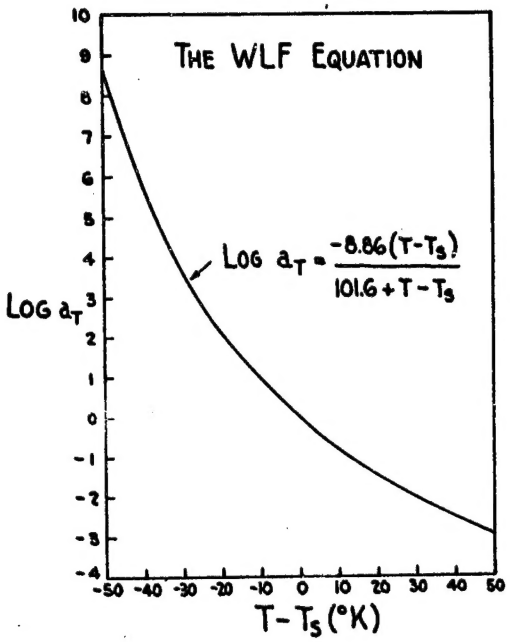

FIGURE 4

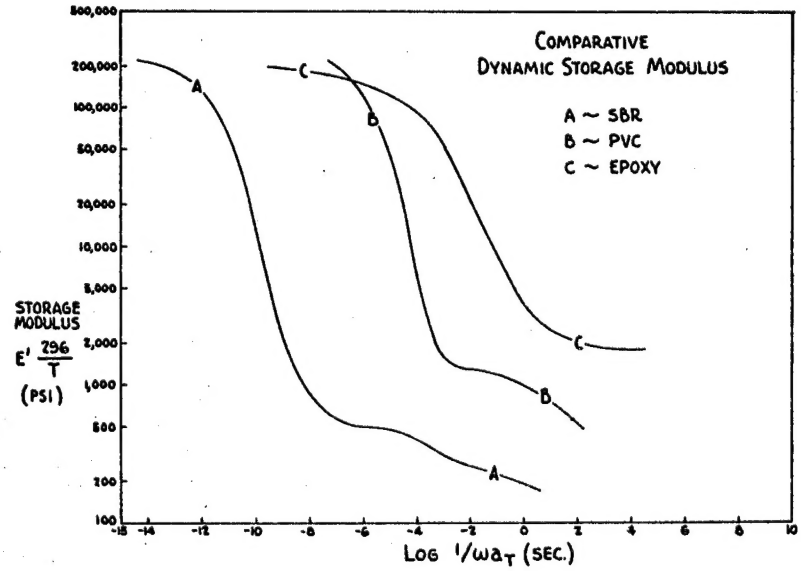

FIGURE 5

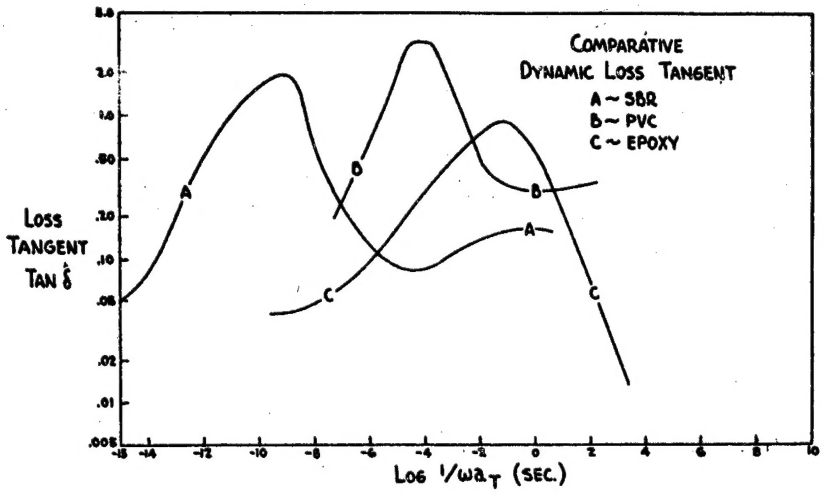

FIGURE 6

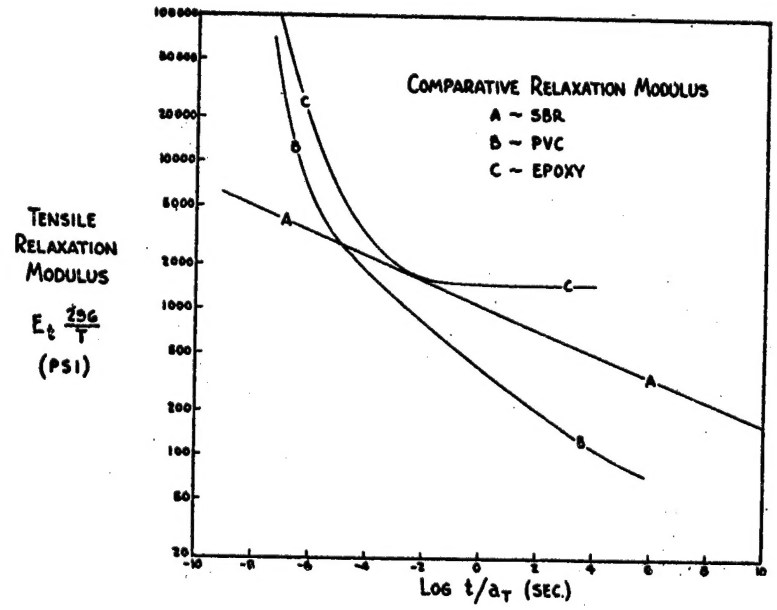

FIGURE 7

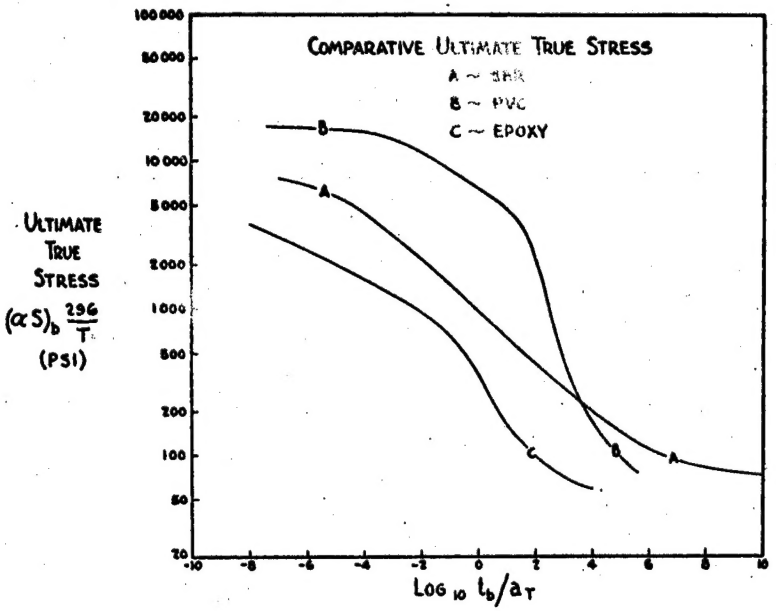
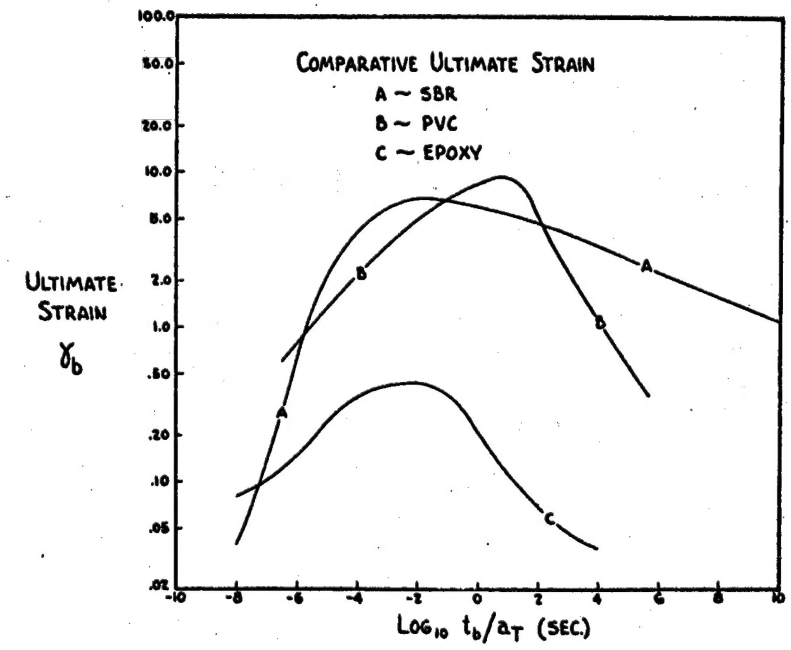
FIGURE 8